Electrochemical study of selenium (IV) mediated by carbon nanotubes modified glassy carbon electrode in blood medium

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Abstract

Sodium selenite Se(IV) was studied by cyclic voltammetric technique to identify the extent of its effect on both normal saline and blood medium components as oxidative or antioxidative reagent. Carbon nanotube (CNT) was used to modify glassy carbon electrode (GCE) for the enhancement of redox current peaks. It was found from the results of the study that reduction current peak of Se(IV) in blood medium appears at -1V in 0.1 mM of sodium selenite, but the reduction current peak disappears when adding more amount of Se(IV) to the blood which causes enhancement of the oxidation current peak of Se(IV) at 0.25 V in 10 mM of sodium selenite. Ascorbic acid (AA) was affected on the redox current peaks of Se(IV) in blood medium that enhanced the cathodic current peak and disappearing the anodic current peak. So sodium selenite considered as antioxidative material at low concentration in blood medium and become oxidative in high concentration especially in presence of AA.

Keywords: cyclic voltammetry, carbon nanotube, glassy carbon electrode, blood medium, sodium selenite, normal saline

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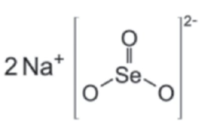
1. Introduction

Scientists used a new method of electrochemical analysis using cyclic voltammetric technique for infected blood pollution which cause of many diseases by blood complexation of the component act as poisoning [1-7].

Selenium (IV) ions in the compound of sodium selenite (Na_2SeO_3) were shown in scheme (1). Most of selenium salts are toxic in high concentrations and the chronic toxicity dose for human beings is about 2.4 to 3.0 milligrams of selenium per day [8, 9].



(1)

Cyclic voltammetric technique was used for the determination of the selenium electrodeposition onto GCE in sulphuric acid medium. Thin layer of Se on the GCE modified working electrode comparing with GCE bar for determination of some electrochemical parameters such as charge transfer rate values with good results at modified GCE which selenium act as electro catalyst [10].

Cathodic stripping voltammetry was used for the determination of selenium in natural waters in present of rhodium. A high detection limit of 2.4pM Se(IV) was found in this technique [11].

Square wave anodic stripping voltammetric technique was used for the determination of selenium(IV) by microfabrication array of gold ultramicroelectrodes which show a good rapid, sensitive and reproducible response for selenium ions [12].

A new mechanism of selenium electrodeposition from H_2SO_4 solution on different substrates such as gold, silver and copper electrodes was studied for reduction current peaks of selenous acid and confirms the mechanism of the deposition process [13].

Cyclic voltammetry and differential pulse voltammetry were used for the electrochemical characterization of azulene selenium compound [14].

Se(IV) ions in acid medium was studied by dropping mercury electrode technique to observe three voltammetric reduction current peaks of H_2SeO_3, HgSe and H_2Se which studied the behavior of Se(IV) on cyclic scanning [15].

The reversible of oxidation–reduction process of Se(IV)/(VI) was determined by cyclic voltammetric technique by the following reaction [16]:

$$SeO_4^{2-} + 2H^+ + 2e^- = SeO_3^{2-} + H_2O \qquad (2)$$

Cyclic voltammetry and cathodic linear stripping voltammetry were used for the determination of selenium deposition by sulfate solution on gold electrode. The results found Se(0)/(2-) reduction current peak which are related to the surface limited phenomena of selenium process [17].

The Se(VI)/(IV) reaction was investigated by cyclic voltammetry to find the oxidation–reduction potential as in the following reaction [18]:

$$SeO_4^{2-} + 2H^+ + 2e^- \rightleftharpoons SeO_3^{2-} + H_2O \quad (3)$$

$$E^0(SeO_4^{2-}/SeO_3^{2-}) = 0.8227 \pm 0.0032\ V \quad (4)$$

$$\varepsilon(SeO_4^{2-},\ Na^+) - \varepsilon(SeO_3^{2-},\ Na^+) = 0.59 \pm 0.12\ kg\ mole^{-1} \quad (5)$$

Selenium nanoparticles were deposited on working electrode using cyclic voltammetric technique to study specific capacitance of 21.98 Fg^{-1} with 91% electrochemical stability [19].

Selenium was electrodeposited on gold substrates by HNO_3 solution using cyclic voltammetric technique. It was found that the reduction of Se^{2+} to Se^0 occurs by electron mechanism at more negative potential [20].

The potential of Se(VI/IV) was studied in high pH by cyclic voltammetric technique, and the results found that E^0 (SeO_4^{2-}/SeO_3^{2-}) = 0.8227 ± 0.0032 V, Δε = 0.59 ± 0.12 kg/mol [21].

In this work sodium selenite in different electrolytes including blood medium was studied by cyclic voltammetric technique using GCE modified with CNT for the determination of electrochemical properties of Se(IV) in blood medium.

2. Experimental

2.1. Reagents and chemicals

Sodium selenite from Thomas Baker (India), normal saline (0.9% NaCl W/V) from Alcon Parenterals (India) Ltd, ascorbic acid (AA) from Technicon chemicals Co. (Oreq Tournai Belgique), healthy human blood samples was received from Iraqi blood bank in Baghdad city of medicine, and other chemicals and solvents were of annular grade and used as received from the manufacturer. Deionized distilled water was used for the preparation of aqueous solutions.

2.2. Preparation of modified glassy carbon electrode

Glassy carbon working electrode modified with carbon nanotube using attachment method to become CNT/GCE was used in this work after cleaning by polishing the surface of GCE with alumina powder and deionized distilled water [22,23].

2.3. Apparatus and procedures

Instruments: EZstat series (potentiostat/galvanostat) NuVant Systems Inc. pioneering electrochemical technologies USA. Electrochemical workstations of Bioanalytical system with potentiostat driven by electroanalytical measuring software was connected to personal computer to perform Cyclic Voltammetry (CV). Ag/AgCl (3M NaCl) and platinum wire (1 mm diameter) was used as a reference and counter electrode, respectively. The glassy carbon working electrode (GCE) was used in this study after cleaning with alumina powder.

Procedure: cyclic voltammetric cell was used in this technique by adding 10 ml of electrolyte (human blood samples) in the quartz cell and immerse three electrodes in the blood medium (GCE as working electrode or GCE modified with CNT, Ag/AgCl reference electrode and counter electrode), then the electrodes was connected with potentiostat to find the results by the cyclic voltammogram using a personal computer.

3. Results and discussion

3.1. Enhancement study

Fig. 1 shows the cyclic voltammogram of Se(IV) in normal saline with different electrodes. It was found that glassy carbon electrode modified with carbon nanotube enhanced the oxidation current peak of Se(IV) about two times which act as electro-catalyst in the different electrolytes. It is very important to use nano-sensors like CNT/GCE in this study for the determination of low detection limit selenium compounds in blood medium which can determine the accuracy of the Se(IV) concentration in the electrolytes.

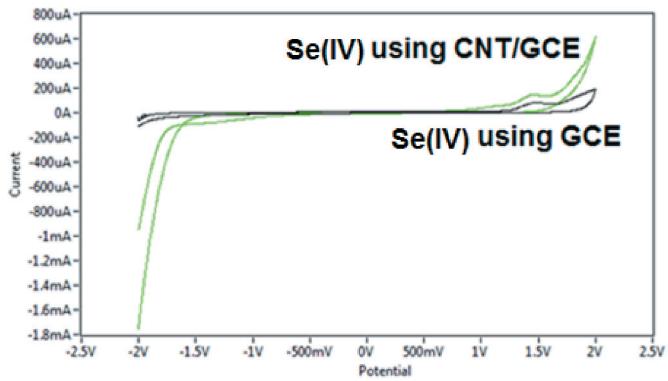


Fig. 1. Cyclic voltammogram of Se(II) in normal saline at GCE and CNT/GCE as working electrodes and Ag/AgCl as reference electrode, scan rate 100 mVsec^{-1}.
1. ábra Se(II) ciklikus voltammogramja normál nyálban; mérő elektródák: GCE és CNT/GCE, referencia elektróda: Ag/AgCl, adatrögzítési sebesség: 100 mVsec^{-1}.

3.2. Effect of Se(IV) on blood medium

In previous studies conducted by researchers, the effect of sodium selenite on the blood of animals in terms of RBC account and the poisoning due to exposure to doses of selenium salts were studied [24, 25]. In the current study, a new method was used to determine the effect of sodium selenite in blood medium using electrochemical method to detect the effect of different concentrations through the oxidation-reduction current peaks in blood medium. *Fig. 2* shows the effect of low concentration of 0.1 mM Se(IV) in blood medium by appearing of reduction peak at -1V, and high concentration of 10 mM Se(IV) which finding a new phenomenon by disappearing of the reduction peak and appearing the oxidation current peak at 0.25 V. This means that low concentration of selenium ions act as antioxidant in blood medium and the high concentration of selenium ions causes oxidation of the blood components as illustrated in the following equation:

$$SeO_3^{4-} + 2e = SeO_3^{2-} \qquad E=0.25V \quad (6)$$

From *Table 1* it was found that the effect of low concentrations of sodium selenite in blood medium act as antioxidant reagent, but when increasing the concentration of selenite from 1.6 mM and above the reduction current peak disappears and enhances the oxidation current peaks.

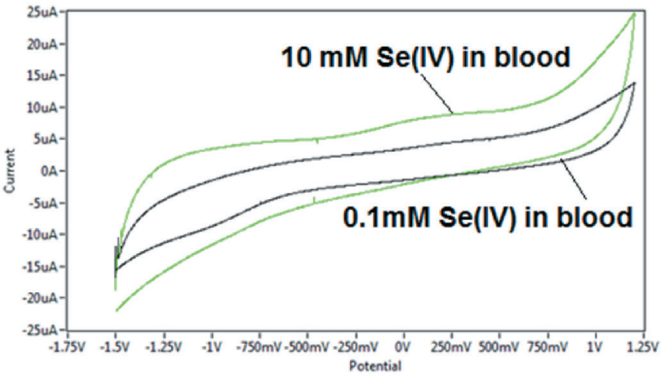


Fig. 2. *Cyclic voltammogram of 0.1 mM Se(IV) and 10 mM Se(IV) in blood medium at CNT/GCE as modified electrode and Ag/AgCl as reference electrode, at scan rate 100 mVsec^{-1}.*

2. ábra *0.1 mM Se(IV) és 10 mM Se(IV) ciklikus voltammogramja vér közegben; mérő elektróda: CNT/GCE, referencia elektróda: Ag/AgCl, adatrögzítési sebesség: 100 mVsec^{-1}.*

3.3. Effect ascorbic acid on Se(IV) in blood medium

The results of previous researches after using the treatment of N-acetyle L-cystine is a substitute for glutathione due to selenium toxicity [26, 27].

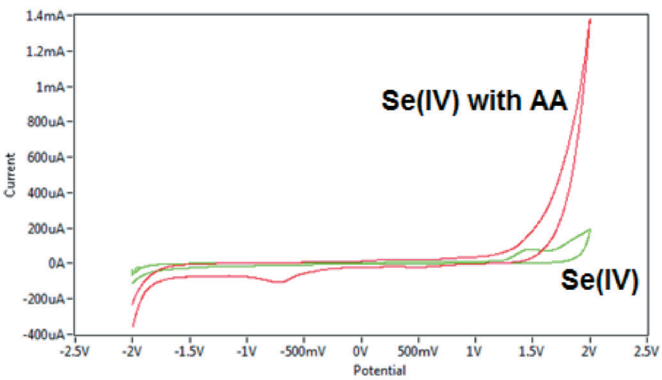


Fig. 3. *Cyclic voltammogram of 0.3 mM Se(II) with AA and without AA in normal saline at CNT/GCE as modified electrode and Ag/AgCl as reference electrode, at scan rate 100 mVsec^{-1}.*

3. ábra *0.3 mM Se(II) ciklikus voltammogramja normál nyálban, aszkorbinsav jelenlétében és anélkül; mérő elektróda: CNT/GCE, referencia elektróda: Ag/AgCl, adatrögzítési sebesség: 100 mVsec^{-1}.*

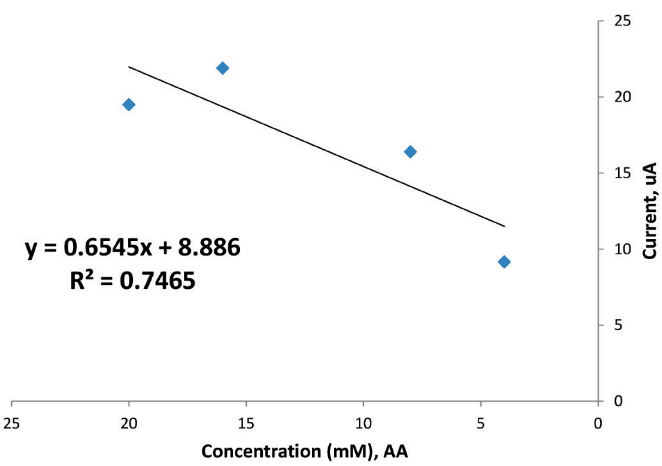


Fig. 4. *Plot of the cathodic current peaks against the different concentrations of AA with 40 mM of sodium selenite in blood medium.*

4. ábra *Katódos áramerősség csúcsértékek 40 mM nátrium-szelenitre vonatkozóan vér közegben, az aszkorbinsav koncentráció függvényében ábrázolva.*

It was found in this study that it is good treatment to prevent the oxidative stress of Se(IV) in blood medium by using ascorbic acid (AA) as antioxidative reagent for Se(IV) in blood medium as shown in *Fig. 3*. Results illustrate that oxidation current peak of Se(IV) appears at 1.5 V in the absence of AA, but it can be clearly seen that the oxidation current peak of Se(IV) disappears when using AA and enhances the reduction current peak of Se(IV) at -0.75 V. This means that AA acts as antioxidative reagent for Se(IV) in blood medium. Table 1 indicates the relationship between the oxidation current peaks of sodium selenite with different concentrations of AA in blood medium. The oxidative stress appears for Se(IV) on the blood component especially in the presence of AA as shown in *Fig. 4*. It means that AA acts as electrochemical catalyst for Se(IV) in blood medium and enhances the oxidation effect of selenite in blood medium.

Na_2SeO_3, mM	Ipa, uA	Epa, V	Ipc, uA	Epc V
0.4	-	-	8.86	-1
0.8	-	-	8.69	-0.985
1.2	-	-	8.48	-0.848
1.6	3.97	0.123	-	-
2	3.92	0.192	-	-
2.4	3.78	0.152	-	-
2.8	3.97	0.46	-	-
3.2	3.97	0.146	-	-
3.6	4.11	0.15	-	-
4	4	0.115	-	-
8	8.74	0.186	-	-
12	5.77	0.018	-	-
16	5.77	0.014	-	-
20	5.77	0.073	-	-
24	5.68	0.056	-	-
28	5.52	0.063	-	-
32	5.59	0.074	-	-
36	5.59	0.074	-	-
40	5.59	0.027	-	-
44	5.94	0.02	-	-
AA, mM				
4	-	-	9.16	0.033
8	-	-	16.40	0.198
12	-	-	-	-
16	-	-	21.90	0.063
20	-	-	19.50	0.054

Table 1 *Oxidation-reduction current peaks and potentials of sodium selenite in blood medium, and with AA.*

1. táblázat *Oxidáció-redukció áramerősség csúcsértékek és potenciálkülönbségek nátrium-szelenitre vonatkozóan vér közegben, aszkorbinsav jelenlétében.*

4. Conclusions

Sodium selenite was studied by voltammetric technique. It can be concluded that it is toxic in blood medium as oxidizing reagent at high concentrations and can be considered as antioxidant at low concentrations. Also, it was found that ascorbic acid solution acts as antioxidizing reagent for Se(IV) in blood medium which causes enhancement of reduction current peak of Se(IV) and causes the oxidation current peak to disappear in blood medium, so traces of selenium compounds is very important for human body especially in blood components.

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Szén nanocsövekkel módosított üvegszerű szén elektródával közvetített szelén (IV) elektrokémiai vizsgálata vér közegben

Nátrium-szelenit Se(IV) ciklikus voltammetriai vizsgálatát mutatja be a cikk nyál és vér közegben, az oxidatív vagy antioxidatív hatás megfigyeléseiről. A redox áramerősség csúcsértékek változását szén nanocsövekkel módosított üvegszerű szén elektródával mérték. Az eredmények szerint Se(IV) redukciós áramerősség csúcsérték mutatható ki -1V-on a 10 mM nátrium-szelenit koncentráció mellett. Aszkorbinsav adagolása erősíti a katódos áramerősség csúcsértékeket és eltünteti az anódos áramerősség csúcsértékeket. A nátrium-szelenit antioxidatív hatású vér közegben kis koncentráció esetén és oxidatív hatású nagy koncentráció esetén, különösen aszkorbinsav jelenlétében.

Kulcsszavak: ciklikus voltmérés, szén nanocső, üvegszerű szén elektróda, vér, nátrium-szelenit, nyál